

Claims

1. A phosphorus- and metal components-containing MFI-structured molecular sieve having a formula expressed in an anhydrous form and on the basis of oxide weight, as follows: (0~0.3) Na₂O (0.5~5.5) Al₂O₃ (1.3~10) P₂O₅ (0.7~15) M1_xO_y (0.01~5) M2_mO_n (70~97) SiO₂, wherein M1 is one of metals selected from the group consisting of Fe, Co and Ni; x represents the atom number of M1; y represents a number required by the oxidation state of M1; M2 is one selected from the group consisting of Zn, Mn, Ga and Sn; m represents the atom number of M2; and n represents a number required by the oxidation state of M2.
2. The molecular sieve according to claim 1 having a formula expressed in an anhydrous form and on the basis of oxide weight as follows: (0~0.2) Na₂O (0.9~5.0) Al₂O₃ (1.5~7) P₂O₅ (0.9~10) M1_xO_y (0.5~2) M2_mO_n (82~92) SiO₂.
3. The molecular sieve according to claim 1 or 2 wherein said M1 is Fe and M2 is Zn.
4. The molecular sieve according to claim 1 or 2 wherein said M1 is Fe and M2 is Mn.
5. The molecular sieve according to claim 1 or 2 wherein said M1 is Fe and M2 is Ga.
6. The molecular sieve according to claim 1 or 2 wherein said M1 is Fe and M2 is Sn.
7. The molecular sieve according to claim 1 or 2 wherein said M1 is Co and M2 is Mn.
8. The molecular sieve according to claim 1 or 2 wherein said M1 is Ni and M2 is Mn.
9. The molecular sieve of claim 1 which is ZSM-5 molecular sieve.
10. Use of the molecular sieve of any one of claims 1~9 as a shape-selective active component in catalysts or additives for catalytic cracking of petroleum hydrocarbons.
11. A process for preparing a phosphorus- and metal components-containing MFI-structured molecular sieve according to any one of claims 1 to 9, characterized by the steps of:

ion-exchanging the Na-type molecular sieve having a MFI structure in a weight ratio of molecular sieve : ammonium salt : $H_2O=1 : (0.1\sim 1) : (5\sim 10)$ at a temperature from room temperature to $100^{\circ}C$ for 0.3~1 hours;

filtering;

- 5 introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve, wherein M1 is one of metals selected from the group consisting of Fe, Co, Ni, and M2 is one of metals selected from the group consisting of Zn, Mn, Ga and Sn; and calcining at $400\sim 800^{\circ}C$ for 0.5-8 hrs.

10 12. A process according to claim 11 wherein said calcining step is carried out under a water vapor atmosphere.

13. A process according to claim 11 wherein said modification is carried out by impregnating or ion-exchanging.

15 14. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously the ammonium-exchanged filter cake with an aqueous solution having a calculated amount of a phosphorus-containing compound at a temperature from room temperature to $95^{\circ}C$, oven-drying the resultant slurry, calcining the dried solid at $400\sim 800^{\circ}C$, then mixing homogeneously the calcined solid with an aqueous solution having a calculated
20 amount of a compound containing metal M1 and a compound containing metal M2 at a temperature from room temperature to $95^{\circ}C$, and oven-drying the resultant mixture.

25 15. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously the ammonium-exchanged filter cake with an aqueous solution having a calculated amount of a phosphorus-containing compound at a temperature from room temperature to $95^{\circ}C$, oven-drying the resultant slurry, calcining the dried solid at $400\sim 800^{\circ}C$, then mixing homogeneously the calcined solid with an aqueous solution having a calculated
30 amount of a compound containing metal M1 at a temperature from room temperature to $95^{\circ}C$, and oven-drying the resultant mixture; calcining the dried solid at $400\sim 800^{\circ}C$, finally mixing homogeneously the calcined solid with an

aqueous solution having a calculated amount of a compound containing metal M2 at a temperature from room temperature to 95°C, and oven-drying the resultant mixture, wherein the two metal components to be supported may be also added in a reversed sequence.

5 16. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously the ammonium-exchanged filter cake with an aqueous solution having a calculated amount of a phosphorus-containing
10 resultant slurry, then mixing homogeneously it with an aqueous solution having a calculated amount of a compound containing metal M1 and a compound containing metal M2 at a temperature from room temperature to 95°C, and oven-drying the resultant mixture, wherein the two metal components to be supported may be also added in a reversed sequence.

15 17. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously the ammonium-exchanged filter cake with an aqueous solution having a calculated amount of a phosphorus-containing
20 resultant slurry, then mixing homogeneously it with an aqueous solution having a calculated amount of a compound containing metal M1 at a temperature from room temperature to 95°C, and oven-drying the resultant mixture; and finally mixing homogeneously it with an aqueous solution having a calculated amount of a compound containing metal M2 at a temperature from room temperature to
25 95°C, and oven-drying the resultant mixture, wherein the two metal components to be supported may be also added in a reversed sequence.

30 18. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously the ammonium-exchanged filter cake with an aqueous solution having a calculated amount of a phosphorus-containing compound, a compound containing metal M1 and a compound containing metal M2 at a temperature from room temperature to 95°C, and oven-drying the

resultant slurry.

19. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously said ammonium-exchanged filter cake with
5 an aqueous solution having a calculated amount of a phosphorus-containing compound at a temperature from room temperature to 95°C, oven-drying the resultant slurry, calcining the dried solid at 400~800°C, and after mixing homogeneously the calcined solid with an aqueous solution having a calculated amount of a compound containing metal M1 and a compound containing metal
10 M2 in a solid : liquid ratio of 1 : (5 ~ 20), stirring the resultant mixture at 80~95°C and pH 4~7 for 2~3 hours, and then filtering the mixture, wherein the ion-exchange may be repeated for many times, and the exchanged sample may be washed with water for many times before oven-drying the washed sample.

20. A process according to any one of claims 14 to 19 wherein said
15 phosphorus-containing compound is one selected from the group consisting of phosphoric acid, ammonium hydrogen phosphate, ammonium dihydrogen phosphate or ammonium phosphate or a mixture thereof.

21. A process according to any one of claims 14 to 19 wherein said
20 compound containing metal M1 and said compound containing metal M2 are selected from their water soluble salts.

22. A process according to claim 21 wherein said water soluble salts are one selected from the group consisting of sulfate, nitrate and chloride salt.